

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
6 December 2001 (06.12.2001)

PCT

(10) International Publication Number
WO 01/91815 A2

(51) International Patent Classification⁷: **A61L 15/00**

(21) International Application Number: **PCT/IB01/01057**

(22) International Filing Date: **3 May 2001 (03.05.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
09/584,527 **31 May 2000 (31.05.2000) US**

(71) Applicant: **BASF AKTIENGESELLSCHAFT**
[DE/DE]; 67056 Ludwigshafen (DE).

(72) Inventors: **MITCHELL, Michael, A.; 440 Pheasant Ridge, Lake Zurich, IL 60047 (US). ECKERT, David; 1547 South Meacham Road, Palatine, IL 60067 (US).**

(53) Agent: **BROWN, John, D.; Forrester Ketley & Co., Forrester House, 52 Bounds Green Road, London N11 2EY (GB).**

(81) Designated State (national): **JP.**

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

Published:
— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/91815 A2(54) Title: **SURFACE-TREATED SUPERABSORBENT POLYMER PARTICLES**

(57) **Abstract:** Surface-crosslinked superabsorbent polymer particles are obtained by treating 100 parts by weight of superabsorbent polymer particles with about 0.001 to about 10 parts by weight of an oxazolinium ion. The oxazolinium ion can be formed *in situ* by heating superabsorbent particles treated with an oxazolinium ion precursor, such as a hydroxyalkylamide. A stable oxazolinium ion also can be used to surface crosslink the SAP particle. Surface crosslinking the superabsorbent polymer particles with an oxazolinium ion increases both the rate of liquid absorption and the quantity of liquid absorbed and retained by the superabsorbent particles.

- 1 -

SURFACE-TREATED SUPERABSORBENT POLYMER PARTICLES

CROSS REFERENCE TO RELATED APPLICATIONS

5

This is a continuation-in-part of U.S. patent application Serial No. 09/390,462, filed September 7, 1999, pending.

10

FIELD OF THE INVENTION

The present invention relates to surface-crosslinked superabsorbent polymer particles, and to methods of producing the surface-crosslinked superabsorbent particles. The present invention also relates to the use of the surface-crosslinked particles in articles, such as diapers, catamenial devices, and wound dressings. More particularly, the present invention relates to surface treating superabsorbent polymer (SAP) particles, such as a neutralized, crosslinked, homopolymer or copolymer of acrylic acid, with an oxazolinium ion to substantially improve the water absorption and water retention properties of the SAP particles.

BACKGROUND OF THE INVENTION

Water-absorbing resins are widely used in sanitary goods, hygienic goods, wiping cloths, water-retaining agents, dehydrating agents, sludge coagulants, disposable towels and bath mats, disposable door mats, thickening agents, disposable litter mats for pets, condensation-preventing agents, and controlled release agents for various

- 2 -

chemicals. Water-absorbing resins are available in a variety of chemical forms, including substituted and unsubstituted natural and synthetic polymers, such as hydrolysis products of starch acrylonitrile 5 graft polymers, carboxymethylcellulose, crosslinked polyacrylates, sulfonated polystyrenes, hydrolyzed polyacrylamides, polyvinyl alcohols, polyethylene oxides, polyvinylpyrrolidones, and polyacrylonitriles.

10 Such water-absorbing resins are termed "superabsorbent polymers," or SAPs, and typically are lightly crosslinked hydrophilic polymers. SAPs are generally discussed in Goldman et al. U.S. Patent Nos. 5,669,894 and 5,559,335, the disclosures 15 of which are incorporated herein by reference. SAPs can differ in their chemical identity, but all SAPs are capable of absorbing and retaining amounts of aqueous fluids equivalent to many times their own weight, even under moderate pressure. For example, 20 SAPs can absorb one hundred times their own weight, or more, of distilled water. The ability to absorb aqueous fluids under a confining pressure is an important requirements for an SAP used in a hygienic article, such as a diaper.

25 As used here and hereafter, the term "SAP particles" refers to superabsorbent polymer particles in the dry state, i.e., particles containing from no water up to an amount of water less than the weight of the particles. The term "particles" refers 30 to granules, fibers, flakes, spheres, powders, platelets, and other shapes and forms known to persons skilled in the art of superabsorbent polymers. The terms "SAP gel" and "SAP hydrogel" refer

- 3 -

to a superabsorbent polymer in the hydrated state, i.e., particles that have absorbed at least their weight in water, and typically several times their weight in water. The terms "surface-treated SAP particle" and "surface-crosslinked SAP particle" refer to an SAP particle having its molecular chains present in the vicinity of the particle surface crosslinked by a compound applied to the surface of the particle. The term "surface crosslinking" means that the level of functional crosslinks in the SAP particle in the vicinity of the surface of the particle is generally higher than the level of functional crosslinks in the SAP particle in the interior of the particle.

SAP particles can differ in ease and cost of manufacture, chemical identity, physical properties, rate of water absorption, and degree of water absorption and retention, thus making the ideal water-absorbent resin a difficult composition to design. For example, the hydrolysis products of starch-acrylonitrile graft polymers have a comparatively high ability to absorb water, but require a cumbersome process for production and have the disadvantages of low heat resistance and decay or decomposition due to the presence of starch. Conversely, other water-absorbent polymers are easily and cheaply manufactured and are not subject to decomposition, but do not absorb liquids as well as the starch-acrylonitrile graft polymers.

Therefore, it would be extremely advantageous to provide a method of increasing the water absorption properties of a stable, easy to manufacture SAP particles to match the superior water

- 4 -

absorption properties of a difficult to manufacture particle. Likewise, it would be advantageous to further increase the liquid absorption properties of already superior SAP particles.

5 In addition, conventional SAP particles all have a serious defect in that their rates of liquid absorption are lower than fluff pulp and paper. For example, when urine is excreted on a disposable diaper containing conventional SAP
10 particles, the urine can remain in contact with the skin for a relatively long time and make the wearer uncomfortable. This is attributed to the low rate at which the diaper can absorb urine.

15 Attempts have been made to increase the liquid absorption rate by increasing the surface area of the SAP particle, i.e., by decreasing its particle size. However, when the particle size of the SAP particle is decreased, it generally forms a "fish eye" upon contact with urine, which retards
20 the speed of liquid absorption. When the SAP particles are in the form of granules, each granule constitutes a "fish eye" and the speed of liquid absorption decreases. SAP particles in flake form exhibit a moderate increase in the speed of liquid
25 absorption, but SAP flakes are bulky and are difficult to transport and store.

30 Initially, the swelling capacity of an SAP particle on contact with liquids, also referred to as free swelling capacity, was the main factor in the design and development of SAP particles. Later, however, it was found that not only is the amount of absorbed liquid important, but the stability of the swollen gel, or gel strength, also is important.

- 5 -

The free swelling capacity, on one hand, and the gel strength, on the other hand, represent contrary properties. Accordingly, SAP particles having a particularly high absorbency typically exhibit a 5 poor gel strength, such that the gel deforms under pressure (e.g., the load of a body), and prevents further liquid distribution and absorption.

A balanced relation between absorptivity (gel volume) and gel strength is desired to provide 10 proper liquid absorption, liquid transport, and dryness of the diaper and the skin when using SAP particles in a diaper. In this regard, not only is the ability of the SAP particle to retain a liquid under subsequent pressure an important property, but 15 absorption of a liquid against a simultaneously acting pressure, i.e., during liquid absorption also is important. This is the case in practice when a child or adult sits or lies on a sanitary article, or when shear forces are acting on the sanitary 20 article, e.g., leg movements. This absorption property is referred to as absorption under load.

Currently, there is a trend to reduce the size and thickness of sanitary articles for esthetic and environmental reasons (e.g., reduction of waste 25 in landfills). This is accomplished by reducing the large volume of fluff pulp and paper in diapers, and increasing the amount of SAP particles. The SAP particles, therefore, have to perform additional functions with respect to liquid absorption and 30 transport which previously were performed by the fluff pulp and paper, and which could not be accomplished satisfactorily with conventional SAP particles.

- 6 -

Investigators have researched various methods of improving the amount of liquid absorbed and retained by SAP particles, especially under load, and the rate at which the liquid is absorbed.

5 One preferred method of improving the absorption and retention properties of SAP particles is to surface treat the SAP particles.

The surface treatment of SAP particles is well known. For example, U.S. Patent No. 4,043,952 discloses the use of polyvalent metal compounds as surface treating compounds. U.S. Patent No. 4,051,086 discloses the use of glyoxal as a surface treatment to improve the absorption rate of SAP particles. The surface treatment of SAP particles with crosslinking agents having two or more functional groups capable of reacting with pendant carboxylate or other groups contained on the polymer comprising the SAP particle is disclosed in various patents. The surface treatment improves absorbency and gel rigidity to improve liquid flowability and prevent SAP particle agglomeration, as well as improving gel strength.

20 As disclosed in the art, the SAP particles are either mixed with the surface-crosslinking agent, optionally using small amounts of water and/or an organic solvent, or an SAP hydrogel containing 10% to 40%, by weight, water is dispersed in a hydrophilic or hydrophobic solvent and mixed with the surface-crosslinking agent.

30 Prior surface crosslinking agents include diglycidyl ethers, halo epoxy compounds, polyols, polyamines, polyisocyanates; polyfunctional aziridine compounds, and di- or tri-alkylhalides.

- 7 -

Regardless of the identity of the surface cross-linking agent, the agent used for the surface treatment has at least two reactive functional groups, and the SAP particles are heated after the surface crosslinking agent is applied to the surface of the SAP particles.

Surface-crosslinked SAP particles, in general, exhibit higher liquid absorption and retention values than SAP particles having a comparable level of internal crosslinks, but lacking surface crosslinking. Internal crosslinks arise from polymerization of the monomers comprising the SAP particles, and are present in the polymer backbone. It has been theorized that surface crosslinking increases the resistance of SAP particles to deformation, thus reducing the degree of contact between surfaces of neighboring SAP particles when the resulting hydrogel is deformed under an external pressure. The degree to which absorption and retention values are enhanced by surface crosslinking is related to the relative amount and distribution of internal and surface crosslinks, and to the particular surface crosslinking agent and method of surface crosslinking.

As understood in the art, surface-crosslinked SAP particles have a higher level of crosslinking in the vicinity of the surface than in the interior. As used herein, "surface" describes the outer-facing boundaries of the particle. For porous SAP particles, exposed internal surface also are included in the definition of surface.

Prior methods of performing surface crosslinking of SAP particles are disclosed, for example,

- 8 -

in Obayashi U.S. Patent No. 4,541,871, WO 92/16565, WO 93/05080, Alexander U.S. Patent No. 4,824,901, Johnson U.S. Patent No. 4,789,861, Makita U.S. Patent No. 4,587,308, Tsubakimoto U.S. Patent No. 4,734,478, Kimura et al. U.S. Patent No. 5,164,459, DE 4,020,780, and EPO 509,708. Surface crosslinking of SAPs is generally discussed in F.L. Buchholz et al., ed., "Modern Superabsorbent Polymer Technology," Wiley-VCH, New York, NY, pages 97-108 (1998).

10 A problem encountered in several prior compounds and methods used to surface crosslink SAP particles is the relatively high temperature required to form the surface crosslinks between the SAP and the surface crosslinking agent. Typically, temperatures in excess of 180°C are required to form the surface crosslinks. At such temperatures, the SAP particle has a tendency to degrade in color from white or off-white to tan or brown. Such color degradation provides an SAP particle that is esthetically unacceptable to consumers. In addition, a high surface crosslinking temperature can increase the residual monomer content of the SAP particle, which can lead to adverse environmental and health effects, or can lead to rejection of the SAP particles for failing to meet specifications.

15 20 25 30 The present invention is directed to a more reactive class of crosslinking agents, that does not require the high temperatures or prolonged heating associated with prior surface crosslinking agents. The present invention also is directed to surface-treated SAP particles that overcome the disadvantages associated with the use of prior surface

- 9 -

crosslinking agents and with prior surface cross-linked SAP particles.

SUMMARY OF THE INVENTION

5

The present invention is directed to surface-treated SAP particles and to a method of surface treating SAP particles with a sufficient amount of an oxazolinium ion to substantially improve the water-absorption and water retention properties of the SAP particles. In particular, the present invention is directed to treating SAP particles with oxazolinium ions, which can be formed *in situ*, by applying an oxazolinium ion precursor, such as a hydroxyalkylamide (HAA), to the surface of the SAP particles, then heating the precursor-treated SAP particles at about 90°C to about 170°C for about 60 to about 180 minutes to form the oxazolinium ion, which then surface crosslinks the SAP particles.

25

If the oxazolinium ion has sufficient stability to exist for a prolonged time at room temperature, then SAP particles can be treated with the oxazolinium ion, and the resulting treated particles can be heated to surface crosslink the SAP particles. In this embodiment, the stable oxazolinium ion is sufficiently reactive to surface crosslink the SAP particles at a temperature of about 90°C to about 170°C.

30

In accordance with the present invention, SAP particles possess improved water absorption and water retention properties as a result of surface treatment with an oxazolinium ion. Treatment with

- 10 -

an oxazolinium ion is especially effective when performed on polyacrylate salts, hydrolyzed polyacrylamides, or other polymers having a plurality of pendent neutralized carboxyl groups.

5 Therefore, the present invention is directed to surface-treated SAP particles having about 0.001 to about 10 parts by weight of an oxazolinium ion, or oxazolinium ion precursor, per 100 parts by weight of SAP particles, applied to the 10 surfaces of the SAP particles to crosslink molecular chains existing at least in the vicinity of the surface of the SAP particles.

15 One aspect of the present invention is to provide such surface-treated SAP particles, and to a method of manufacturing the surface-treated SAP 20 particles comprising applying a sufficient amount of an HAA to surfaces of the SAP particles and heating the surface-treated SAP particles at a sufficient temperature and for a sufficient time for the HAA to form an oxazolinium ion, which reacts with pendent groups on a polymer comprising the SAP particle to 25 form surface crosslinks on the SAP particle.

30 Yet another aspect of the present invention is to provide a method of surface crosslinking SAP particles comprising applying a sufficient amount of an oxazolinium ion to surfaces of the SAP particles and heating the surface treated SAP particles at about 90°C to about 170°C for about 60 to about 180 minutes for the oxazolinium ion to 35 surface crosslink the SAP particles.

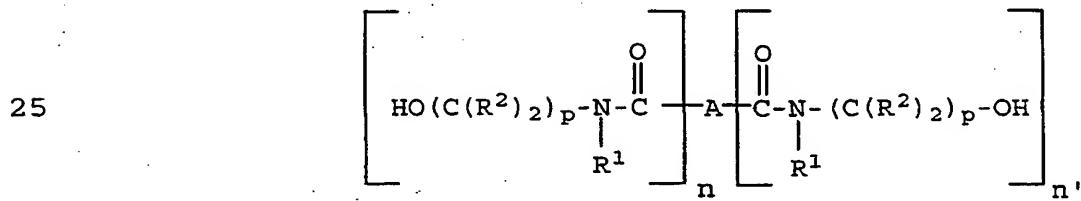
Another aspect of the present invention is to provide a method of surface treating SAP particles comprising heating a sufficient amount of an

- 11 -

HAA in the presence of the SAP particles at a sufficient temperature (e.g., about 100°C to about 160°C and for a sufficient time (e.g., about 90 to about 150 minutes) for the HAA to cyclize and thereby form an oxazolinium ion, which then surface crosslinks the SAP particles.

Yet another aspect of the present invention is to provide surface-treated SAP particles exhibiting a high retention capacity, high gel strength, and high absorbency under load. This aspect is achieved by exposing a particle-shaped SAP to about 0.001% to about 10% by weight of an oxazolinium ion, either formed *in situ* by heating an HAA in the presence of SAP particles, or by applying an oxazolinium ion to the particles, and heating to about 90°C to about 170°C.

Another aspect of the present invention is to provide an SAP particle having surface crosslinks provided by an oxazolinium ion, which is generated by heating a hydroxyalkylamide (HAA) having the structure:



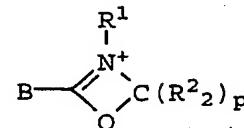
30 wherein A is a bond, hydrogen, or a monovalent or polyvalent organic radical selected from the group consisting of a saturated or unsaturated alkyl radical containing 1 to 60 carbon atoms, aryl, tri-

- 12 -

C_{1-4} alkyleneamino, and an unsaturated radical containing one or more ethylenic groups [$>C=C<$]; R^1 , selected independently, are hydrogen, straight or branched chain C_{1-5} alkyl, or straight or branched chain C_{1-5} hydroxyalkyl; R^2 , selected independently, are radicals selected from the group consisting of hydrogen and straight or branched chain C_{1-5} alkyl, or the R^2 radicals can be joined to form, together with the carbon atoms, a cycloalkyl ring; p and p' , independently, are integers 1 to 4; n is an integer having a value of 1 or 2, and n' is an integer having a value 0 to 2; or when n' is 0, a polymer or copolymer (i.e., n has a value greater than 1, preferably 2 to 10) formed from the hydroxyalkyl-amide when A is an unsaturated radical.

Another aspect of the present invention is to provide an SAP particles having surface cross-links provided by an oxazolinium having the structure:

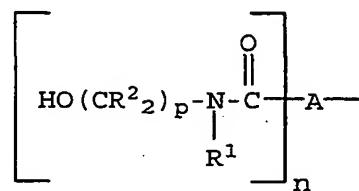
20



25

wherein B is

30



- 13 -

and A, R¹, R², p, p¹, and n are as defined above with respect to an HAA. Such oxazolinium ions are stable at room temperature, and have a counterion such as tosylate, mesylate, or fluoride. The oxazolinium ions are sufficiently reactive to form surface crosslinks on an SAP particle at about 90°C to about 170°C.

Still another aspect of the present invention is to provide SAP particles surface cross-linked with a oxazolinium ion in an amount sufficient to substantially improve the water absorbency and water retention properties of the SAP particles, such as retention capacity, absorption rate, and gel strength, and to maintain a "dry feel" for the SAP particles after significant liquid absorption.

These and other aspects and advantages of the present invention will become apparent from the following detailed description of the preferred embodiments.

20

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, SAP particles are surface treated with an oxazolinium ion to substantially increase the rate of liquid absorption, amount of liquid absorption, and overall retention of liquids by the SAP particles. Surface-treatment of the SAP particles at any time after polymerization and sufficient drying to form solid SAP particles improves liquid absorption properties. For economics and ease of manufacture, the surface treatment is performed most advantageously immediately after the SAP particles are synthesized, dried

- 14 -

to an appropriate water content, and sized, such as by grinding.

As will become apparent from the following detailed description of the preferred embodiments, 5 surface-crosslinking of SAP particles with an oxazolinium ion substantially improves the water absorption properties of the SAP particles, which can be either acidic or basic in nature. Of particular utility are SAP particles containing a 10 plurality of pendant, neutralized carboxyl groups along the polymer chain.

As stated above, the surface treatment of SAP particles is well known. However, many surface crosslinking agents exhibit disadvantages. Some 15 surface crosslinking agents have toxic properties and, therefore, cannot be used in the sensitive field of hygiene because they pose a threat to health or the environment. For example, in addition to the risk of skin irritation, epoxy, glycidyl, 20 isocyanate, and organic halogen compounds, have a sensitizing effect, and frequently have a carcinogenic and mutagenic potential. Polyamines are avoided as surface crosslinking agents because of possible nitrosamine formation. In any case, when 25 used in diapers and other sanitary articles, residual amounts of toxicologically critical crosslinking agents must be removed from the SAP particles, which involves additional process steps and increases the cost of the SAP particles.

30 In addition, a majority of the commonly used surface crosslinking agents required heating at temperatures in excess of 180°C in order to react with the SAP particles and form surface crosslinks.

- 15 -

Heating at such a high temperature can increase the residual monomer content of the surface crosslinked SAP particles. An increased residual monomer content poses both toxicological and environmental 5 concerns, and is unacceptable commercially.

The high temperature required to form surface crosslinks also causes the SAP particles to degrade in color from white or off-white to tan or brown. The tan to brown color of the SAP particles 10 is esthetically unacceptable to consumers, who equate the tan to brown color of the SAP particles to an inferior product. The combination of color degradation and increased residual monomer can lead to SAP particles that do not meet production specifications and, therefore, are refused by the pur- 15 chaser and/or consumer. The present invention over- comes these disadvantages associated with prior sur- face crosslinking agents by utilizing an oxazolinium ion as the surface crosslinking agent for the SAP 20 particles.

The identity of the SAP particles utilized in the present invention is not limited. The SAP particles are prepared by methods well known in the art, for example, solution or emulsion polymeriza- 25 tion. The SAP particles, therefore, can comprise an acidic water-absorbing resin, a basic water-absorb- ing resin, a blend of an acidic and basic water- absorbing resin, or a multicomponent SAP particle as disclosed in WO 99/25393, the disclosure of which is 30 incorporated herein by reference.

The SAP particles are prepared, for example, by:

- 16 -

(1) copolymerizing an acrylate salt and a crosslinking monomer in aqueous solution, and drying the resulting gel-like hydrous polymer by heating;

5 (2) dispersing an aqueous solution of acrylic acid and/or an alkali metal acrylate, a water-soluble radical polymerization initiator, and a crosslinkable monomer in an alicyclic and/or an aliphatic hydrocarbon solvent in the presence of a surface-active agent, and subjecting the mixture to
10 suspension polymerization;

(3) saponifying copolymers of vinyl esters and ethylenically unsaturated carboxylic acids or their derivatives;

15 (4) polymerizing starch and/or cellulose, a monomer having a carboxyl group or capable of forming a carboxyl group upon hydrolysis, and a crosslinking monomer in an aqueous medium, and, as required, hydrolyzing the resulting polymer; or

20 (5) reacting an alkaline substance with a maleic anhydride-type copolymer containing maleic anhydride and at least one monomer selected from α -olefins and vinyl compounds, and, as required, reacting the reaction product with a polyepoxy compound. Other methods and monomers that provide SAP
25 particles also are known in the art.

Generally, acidic water-absorbing resins have carboxylate, sulfonate, sulfate, and/or phosphate groups incorporated along the polymer chain. Polymers containing these acid moieties are synthesized either from monomers previously substituted with one or more of these acidic functional groups or by incorporating the acidic functional group into the polymer after synthesis. To incorporate car-

- 17 -

boxyl groups into a polymer, any of a number of ethylenically unsaturated carboxylic acids can be homopolymerized or copolymerized. Carboxyl groups also can be incorporated into the polymer chain 5 indirectly by hydrolyzing a homopolymer or copolymer of monomers such as acrylamide, acrylonitrile, methacrylamide, and alkyl acrylates or methacrylates.

An acidic water-absorbing resin present in an SAP particle can be either a strong or a weak 10 acidic water-absorbing resin. The acidic water-absorbing resin can be a single resin, or a mixture of resins. The acidic resin can be a homopolymer or a copolymer.

The acidic water-absorbing resin typically 15 is a neutralized, lightly crosslinked acrylic-type resin, such as neutralized, lightly crosslinked polyacrylic acid. The lightly crosslinked acidic resin typically is prepared by polymerizing an acidic monomer containing an acyl moiety, e.g., 20 acrylic acid, or a moiety capable of providing an acid group, i.e., acrylonitrile, in the presence of a free radical crosslinker, i.e., a polyfunctional organic compound. The acidic resin can contain 25 other copolymerizable units, i.e., other monoethylenically unsaturated comonomers, well known in the art, as long as the polymer is substantially, i.e., at least 10%, and preferably at least 25%, acidic monomer units. To achieve the full advantage of the present invention, the acidic resin contains at 30 least 50%, and more preferably, at least 75%, and up to 100%, acidic monomer units. The acidic resin is neutralized at least 50 mole %, and preferably at

- 18 -

least 70 mole %, with a base prior to surface crosslinking.

Ethylenically unsaturated carboxylic acid and carboxylic acid anhydride monomers, and salts, useful in the acidic water-absorbing resin include

5 acrylic acid, methacrylic acid, ethacrylic acid, α -chloroacrylic acid, α -cyanoacrylic acid, β -methylacrylic acid (crotonic acid), α -phenylacrylic acid, β -acryloxypropionic acid, sorbic acid, α -chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid, β -stearylacrylic acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, maleic acid, fumaric acid, tricarboxyethylene, 2-methyl-2-butene dicarboxylic acid, maleamic acid, N-phenyl maleamide, maleamide, maleic anhydride, fumaric anhydride, itaconic anhydride,

10 citraconic anhydride, mesaconic anhydride, methyl itaconic anhydride, ethyl maleic anhydride, diethylmaleate, methylmaleate, and maleic anhydride.

Sulfonate-containing acidic resins can be prepared from monomers containing functional groups hydrolyzable to the sulfonic acid form, for example, alkenyl sulfonic acid compounds and sulfoalkylacrylate compounds. Ethylenically unsaturated sulfonic acid monomers include aliphatic or aromatic vinyl sulfonic acids, such as vinylsulfonic acid, allyl sulfonic acid, vinyl toluene sulfonic acid, styrene sulfonic acid, acrylic and methacrylic sulfonic acids, such as sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, 2-vinyl-4-ethylbenzene, 2-allylbenzene sulfonic acid, 1-phenylethylene sulfonic acid, sulfopropyl methacrylate, 2-hydroxy-3-methacryloxypropyl sulfonic acid, and 2-acrylamide-2-methylpropane sulfonic acid.

- 19 -

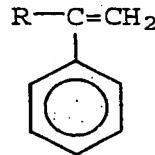
Sulfate-containing acidic resins are prepared by reacting homopolymers or copolymers containing hydroxyl groups or residual ethylenic unsaturation with sulfuric acid or sulfur trioxide.

5 Examples of such treated polymers include sulfated polyvinylalcohol, sulfated hydroxyethyl acrylate, and sulfated hydroxypropyl methacrylate. Phosphate-containing acidic resins are prepared by homopolymerizing or copolymerizing ethylenically unsaturated monomers containing a phosphoric acid moiety, such

10 15 as methacryloxy ethyl phosphate.

Copolymerizable monomers for introduction into the acidic resin, or into the basic resin, include, but are not limited to, ethylene, propylene, isobutylene, C₁ to C₄ alkyl acrylates and methacrylates, vinyl acetate, methyl vinyl ether, and styrenic compounds having the formula:

20



25

wherein R represents hydrogen or a C₁ to C₆ alkyl group, and wherein the phenyl ring optionally is substituted with one to four C₁ to C₄ alkyl or hydroxy groups.

30

Suitable C₁ to C₄ alkyl acrylates include, but are not limited to, methyl acrylate, ethyl acrylate, isopropyl acrylate, n-propyl acrylate, n-butyl acrylate, and the like, and mixtures thereof. Suitable C₁ to C₄ alkyl methacrylates include, but

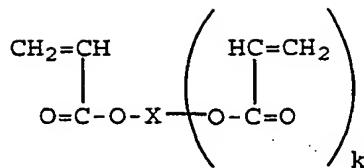
- 20 -

are not limited to, methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, and the like, and mixtures thereof or with C₁₋₄ alkyl acrylates. Suitable styrenic compounds include, but are not limited to, styrene, α -methylstyrene, p-methylstyrene, t-butyl styrene, and the like, and mixtures thereof or with C₁₋₄ alkyl acrylates and/or methacrylates.

As set forth above, polymerization of acidic monomers, and optional copolymerizable monomers, most commonly is performed by free radical processes in the presence of a polyfunctional organic compound. The acidic resins are crosslinked to a sufficient extent such that the polymer is water insoluble. Crosslinking renders the acidic resins substantially water insoluble, and, in part, serves to determine the absorption capacity of the resins. For use in absorption applications, an acidic resin is lightly crosslinked, i.e., has a crosslinking density of less than about 20%, preferably less than about 10%, and most preferably about 0.01% to about 7%.

A crosslinking agent most preferably is used in an amount of less than about 7 wt%, and typically about 0.1 wt% to about 5 wt%, based on the total weight of monomers. Examples of crosslinking polyvinyl monomers include, but are not limited to, polyacrylic (or polymethacrylic) acid esters represented by the following formula (I); and bisacrylamides, represented by the following formula (II).

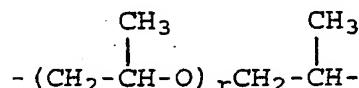
- 21 -



5

(I)

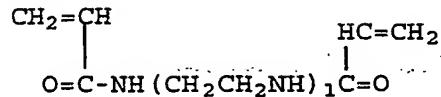
wherein X is ethylene, propylene, trimethylene,
 cyclohexyl, hexamethylene, 2-hydroxypropylene,
 10 $-(\text{CH}_2\text{CH}_2\text{O})_p\text{CH}_2\text{CH}_2-$, or



15

p and r are each an integer 5 to 40, and k is 1 or 2;

20



(II)

25

wherein 1 is 2 or 3.

The compounds of formula (I) are prepared by reacting polyols, such as ethylene glycol, propylene glycol, trimethylolpropane, 1,6-hexane-diol, glycerin, pentaerythritol, polyethylene glycol, or polypropylene glycol, with acrylic acid or methacrylic acid. The compounds of formula (II) are obtained by reacting polyalkylene polyamines,

- 22 -

such as diethylenetriamine and triethylenetetramine, with acrylic acid.

Specific crosslinking monomers include, but are not limited to, 1,4-butanediol diacrylate, 5 1,4-butanediol dimethacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, di-ethyleneglycol diacrylate, diethylene glycol dimethacrylate, ethoxylated bisphenol A diacrylate, ethoxylated bisphenol A dimethacrylate, ethylene glycol dimethacrylate, 1,6-hexanediol diacrylate, 10 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tri-15 propylene glycol diacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, dipentaerythritol pentaacrylate, pentaerythritol tetraacrylate, pentaerythritol triacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, tris(2-hydroxyethyl)isocyanurate tri-20 acrylate, tris(2-hydroxyethyl)isocyanurate trimethacrylate, divinyl esters of a polycarboxylic acid, diallyl esters or a polycarboxylic acid, triallyl terephthalate, diallyl maleate, diallyl fumarate, 25 hexamethylenebismaleimide, trivinyl trimellitate, divinyl adipate, diallyl succinate, a divinyl ether of ethylene glycol, cyclopentadiene diacrylate, tetraallyl ammonium halides, or mixtures thereof. Compounds such as divinylbenzene and divinyl ether 30 also can be used to crosslink the poly(dialkylamino-alkyl acrylamides). Especially preferred crosslinking agents are N,N'-methylenebisacrylamide, N,N'-

- 23 -

methylenebismethacrylamide, ethylene glycol dimethacrylate, and trimethylolpropane triacrylate.

The acidic resin, either strongly acidic or weakly acidic, can be any resin that acts as an SAP in its neutralized form. Examples of acidic resins include, but are not limited to, polyacrylic acid, hydrolyzed starch-acrylonitrile graft copolymers, starch-acrylic acid graft copolymers, saponified vinyl acetate-acrylic ester copolymers, hydrolyzed acrylonitrile copolymers, hydrolyzed acrylamide copolymers, ethylene-maleic anhydride copolymers, isobutylene-maleic anhydride copolymers, poly(vinylsulfonic acid), poly(vinylphosphonic acid), poly(vinylphosphoric acid), poly(vinylsulfuric acid), sulfonated polystyrene, poly(aspartic acid), poly(lactic acid), and mixtures thereof. The preferred acidic resins are the polyacrylic acids.

The final acidic SAP particle contains from about 50 to 100 percent neutralized pendant carboxylate salt units. Accordingly, it may be necessary to neutralize carboxylic acid groups. Neutralization of carboxylic acid groups is accomplished using a strong organic or inorganic base, such as sodium hydroxide, potassium hydroxide, ammonia, ammonium hydroxide, or an organic amine.

The sequence and the number of reactions (e.g., polymerization, hydrolysis, and neutralization) performed to obtain the desired acid functionality attached to acidic resin backbone are not critical. Any number and sequence resulting in a final SAP particle which possesses 0 to about 90 percent copolymerizable monomer units and about 10 to about 100 percent monomer units having pendant

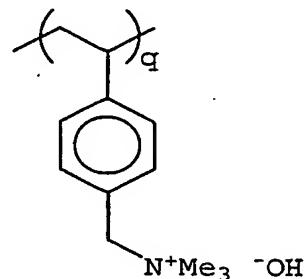
- 24 -

acid groups, and neutralized at least 50 mole %, is suitable.

5 Analogous to the acidic resin, a basic water-absorbing resin present in the SAP particles can be a strong or weak basic water-absorbing resins. The basic water-absorbing resin can be a single resin or a mixture of resins. The basic resin can be a homopolymer or a copolymer. The identity of the basic resin is not limited as long as the basic resin is capable of reacting with an oxazolinium ion. The strong basic resins typically are present in the hydroxide (OH) or bicarbonate (HCO₃) form.

10 The basic water-absorbing resin can be a 15 lightly crosslinked acrylic-type resin, such as a poly(dialkylaminoalkyl (meth)acrylamide). The basic resin also can be a polymer such as a lightly cross-linked polyethylenimine, a poly(vinylamine), a poly-(allylamine), a poly(allylguanidine), a poly(di-20 methyldiallylammonium hydroxide), a quaternized polystyrene derivative, such as

25

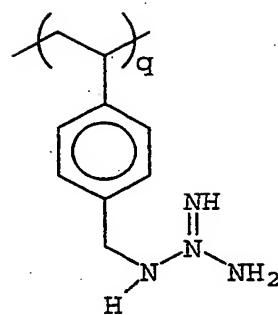


30

a guanidine-modified polystyrene, such as

- 25 -

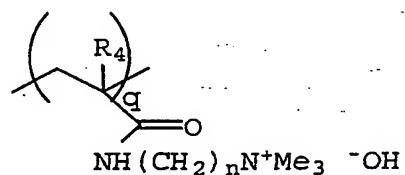
5



10

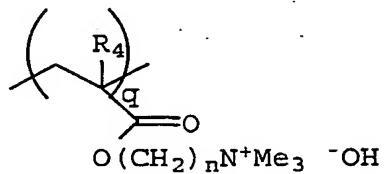
a quaternized poly((meth)acrylamide) or ester analog, such as

15



or

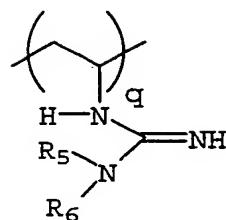
20



25

wherein Me is methyl, R₄ is hydrogen or methyl, n is a number 1 to 8, and q is a number from 10 to about 30 100,000, or a poly(vinylguanidine), i.e., poly(VG), a strong basic water-absorbing resin having the general structural formula (III)

5



(III)

10 wherein q is a number from 10 to about 100,000, and R₅ and R₆, independently, are selected from the group consisting of hydrogen, C₁-C₄ alkyl, C₃-C₆ cycloalkyl, benzyl, phenyl, alkyl-substituted phenyl, naphthyl, and similar aliphatic and aromatic groups. The
 15 lightly crosslinked basic water-absorbing resin can contain other copolymerizable units and is cross-linked using a polyfunctional organic compound, as set forth above with respect to the acidic water-absorbing resin.

20 A basic water-absorbing resin used in the present SAP particles typically contains an amino or a guanidine group. Accordingly, a water-soluble basic resin can be crosslinked in solution by suspending or dissolving an uncrosslinked basic resin
 25 in an aqueous or alcoholic medium, then adding a di- or polyfunctional compound capable of crosslinking the basic resin by reaction with the amino groups of the basic resin. Such crosslinking agents include, for example, multifunctional aldehydes (e.g., glutaraldehyde), multifunctional acrylates (e.g., butanediol diacrylate, TMPTA), halohydrins (e.g., epichlorohydrin), dihalides (e.g., dibromopropane), disulfonate esters (e.g., ZS(O₂)O-(CH₂)_n-OF(O)₂Z,

- 27 -

wherein n is 1 to 10, and Z is methyl or tosyl), multifunctional epoxies (e.g., ethylene glycol diglycidyl ether), multifunctional esters (e.g., dimethyl adipate), multifunctional acid halides (e.g., oxalyl chloride), multifunctional carboxylic acids (e.g., succinic acid), carboxylic acid anhydrides (e.g., succinic anhydride), organic titanates (e.g., TYZOR AA from DuPont), melamine resins (e.g., CYMEL 301, CYMEL 303, CYMEL 370, and CYMEL 373 from Cytec Industries, Wayne, NJ), hydroxymethyl ureas (e.g., N,N'-dihydroxymethyl-4,5-dihydroxyethyleneurea), and multifunctional isocyanates (e.g., toluene diisocyanate or methylene diisocyanate). Crosslinking agents for basic resins also are disclosed in Pinschmidt, Jr. et al. U.S. Patent No. 5,085,787, incorporated herein by reference, and in EP 450 923.

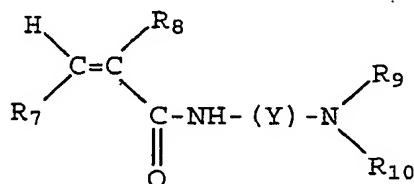
Conventionally, the crosslinking agent is water or alcohol soluble, and possesses sufficient reactivity with the basic resin such that crosslinking occurs in a controlled fashion, preferably at a temperature of about 25°C to about 150°C. Preferred crosslinking agents are ethylene glycol diglycidyl ether (EGDGE), a water-soluble diglycidyl ether, and a dibromoalkane, an alcohol-soluble compound.

The basic resin, either strongly or weakly basic, therefore, can be any resin that acts as an SAP in its charged form. Examples of basic resins include a poly(vinylamine), a polyethylenimine, a poly(vinylguanidine), a poly(allylamine), a poly(allylguanidine), or a poly(dialkylaminoalkyl (meth)-

- 28 -

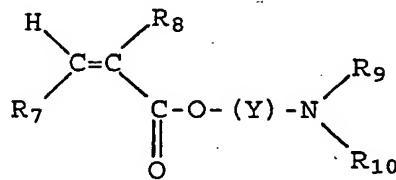
acrylamide) prepared by polymerizing and lightly crosslinking a monomer having the structure

5



10 or its ester analog

15



20 wherein R₇ and R₈, independently, are selected from the group consisting of hydrogen and methyl, Y is a divalent straight chain or branched organic radical having 1 to 8 carbon atoms, R₉ is hydrogen, and R₁₀ is hydrogen or an alkyl radical having 1 to 4 carbon atoms. Preferred basic resins include a poly(vinyl-amine), polyethylenimine, poly(vinylguanadine), poly(methylaminoethyl acrylamide), and poly(methyl-aminopropyl methacrylamide).

30 There is no particular restriction on the shape of the SAP particles used in this invention. The SAP particles can be in the form of spheres obtained by inverse phase suspension polymerization, flakes obtained by drum drying, or irregularly

shaped particles obtained by pulverizing solid polymer. From the standpoint of the speed of absorption, the SAP particles preferably are small, and typically the particle size is about 20 to about 5 2000 μm , preferably about 50 to about 850 μm .

The SAP particles, comprising an acidic resin, basic resin, a blend of acidic and basic resin, or multicomponent SAP particles, are surface treated by applying a surface crosslinking agent to 10 the surface of the SAP particles, followed by heating the particles. Surface treatment results in surface crosslinking of the SAP particles. It has been found that surface treating SAP particles with an oxazolinium ion, either directly or through an 15 oxazolinium ion precursor, enhances the ability of the SAP particles to absorb and retain aqueous media under a load.

In general, surface crosslinking is achieved by contacting SAP particles with a solution 20 of an HAA or a stable oxazolinium ion that wets predominantly only the outer surfaces of the SAP particles. Surface crosslinking of the SAP particles then is performed, preferably by heating at least the wetted surfaces of the SAP particles. 25 Heating the HAA forms oxazolinium ions *in situ*, which in turn surface crosslink the SAP particles. For oxazolinium ions having sufficient stability, the oxazolinium ion can be applied to the outer surfaces of the SAP particles, followed by heating 30 the SAP particles to surface crosslink the exposed surface of the SAP particles.

The surface crosslinking agent utilized in the present invention is an oxazolinium ion. Simple

- 30 -

oxazolinium ions have been isolated and characterized as disclosed in Stanssens et al., *Proc.-Int. Conf. Org. Coat. Sci. Technol.*, p. 435 (1992).

Reactions of oxazolinium ions with carboxylate anions to form esters of 2-hydroxyalkylamides have been disclosed in Winstein et al., *J. Am. Chem. Soc.*, 72, p. 4669 (1950), and McLasland et al., *J. Am. Chem. Soc.*, 72, p. 2190 (1950). Reactions of oxazolinium ions with carboxylic acids to form esters of 2-hydroxyalkylamides have been disclosed in Wicks et al., *J. Coat. Tech.*, 57, p. 51 (1985).

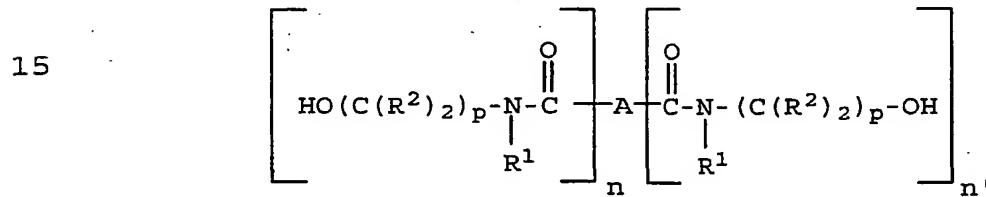
The term "stable oxazolinium ion" is defined herein as an oxazolinium ion that is stable at room temperature and has sufficient reactivity with acidic (e.g., carboxyl) and basic (e.g., amino) moieties at about 90°C to about 170°C to form covalent bonds. Stability is imparted to an oxazolinium ion by judicious selection of a counterion, for example, a counterion comprising a conjugate base of an acid having a pKa of about 1.5 to about 6, preferably a pKa of about 2 to about 5, and most preferably about 2.5 to about 4.5. To achieve the full advantage of the present invention, the counterion is a conjugate base of an acid having a pKa of about 2.5 to about 3.5. Specific examples of counterions include, but are not limited to, benzoate, haloacetate, formate, fluoride, sulfonate (e.g., tosylate or mesylate), and the like.

The reactivity of a stable oxazolinium ion can be increased by exposing the stable oxazolinium ion to a sufficiently polar solvent (e.g., propylene glycol), optionally containing a sufficient concentration of a less acidic counterion to solvate or

- 31 -

exchange the ion pair. The reactivity of a stable oxazolinium ion can be increased prior to heating in the presence of the SAP particles to facilitate the surface crosslinking of the exposed surface of the SAP particles.

The oxazolinium ion surface crosslinking agent utilized in the present invention can be generated *in situ* from a hydroxyalkylamine. Hydroxyalkylamides are disclosed in Swift et al. U.S. Patent No. 4,076,917. An HAA useful in the present invention has the following formula:



20 wherein A is a bond, hydrogen, or a monovalent polyvalent organic radical selected from the group consisting of a saturated or unsaturated alkyl radical contain 1 to 60 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, eicosyl, triacontyl, tetacontyl, pentacontyl, hexylcontyl, and the like, aryl, for example, mono- and dicyclic aryl, such as phenyl, naphthyl, and the like, tri-C₁₋₄ alkyleneamino, such as trimethyleneamino, triethyleneamino, and the like, and an unsaturated radical containing one or more ethylenic groups [>C=C<], such as ethenyl, 1-methylethenyl, 3-butenyl-1,3-diyl, 2-propenyl-1,2-diyl, carboxy C₁₋₄ alkenyl, such as 3-carboxy-2-

25

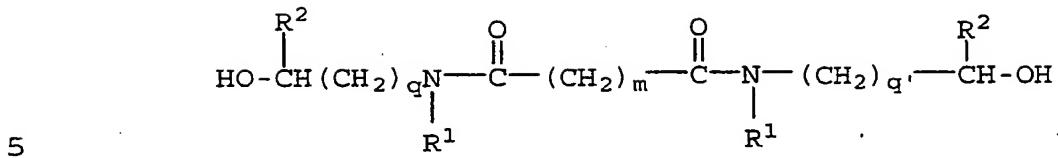
30

- 32 -

propenyl, and the like, C_{1-4} alkoxy carbonyl lower alkenyl, such as 3-methoxycarbonyl-2-propenyl, and the like; R^1 , selected independently, are hydrogen, straight or branched chain C_{1-5} alkyl, such as 5 methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, pentyl, and the like, or straight or branched chain C_{1-5} hydroxyalkyl, such as hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl, 4-hydroxybutyl, 3-hydroxybutyl, 2-hydroxy-2-methylpropyl, 5-hydroxy-10 pentyl, 4-hydroxypentyl, 3-hydroxypentyl, 2-hydroxypentyl, and the isomers of pentyl; R^2 , selected independently, are radicals selected from the group consisting of hydrogen and straight or branched C_{1-5} alkyl, or the R^2 radicals can be joined to form, 15 together with the carbon atoms, a cycloalkyl ring, such as cyclopentyl, cyclohexyl, and the like; p and p' , independently, are an integer 1 to 4; n is an integer having a value of 1 or 2, and n' is an integer having a value of 0 to 2, or when n' is 0, a 20 polymer or copolymer (i.e., n has a value greater than 1, preferably 2-10) formed from the β -hydroxy-alkylamide when A is an unsaturated radical.

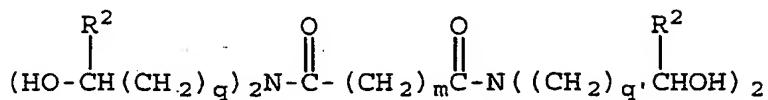
Preferred HAAs are wherein R^1 is H or C_{1-5} hydroxyalkyl, n and n' are each 1, -A- is $-(CH_2)_m-$, 25 m is 0-8, preferably 2-8, each R^2 on the α -carbon is H, and one of the R^2 radicals on the beta carbon in each case is H and the other is H or a C_{1-5} alkyl, and q and q' , independently, are an integer 1 to 3; that is,

- 33 -



Most preferred HAAs have the formula:

10

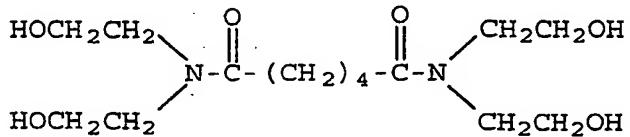


15

wherein both R^2 groups are H or both R^2 groups are $-\text{CH}_3$.

20 Specific examples of HAA compounds include, but are not limited to, bis[N,N-di(β -hydroxyethyl)]adipamide, bis[N,N-di(β -hydroxypropyl)]succinamide, bis[N,N-di(β -hydroxyethyl)]-azelamide, bis[N,N-di(β -hydroxypropyl)]adipamide, and bis[N-methyl-N- (β -hydroxyethyl)]oxamide. A 25 commercially available β -HAA is PRIMID™ XL-552 from EMS-CHEMIE, Dornat, Switzerland. PRIMID™ XL-522 has the structure

30

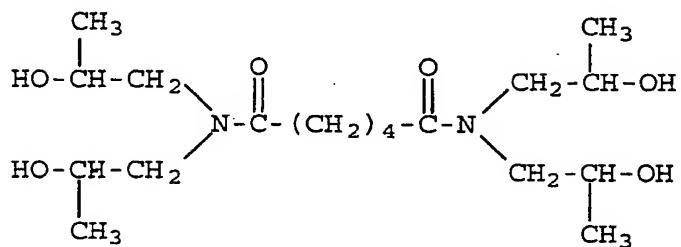


- 34 -

Another commercially available HAA is PRIMID™ QM-1260 from EMS-CHEMIE, having the structure:

5

10



10

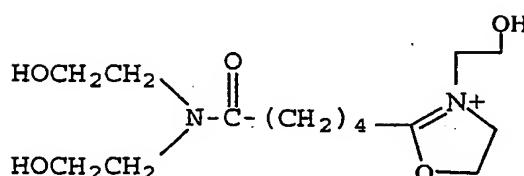
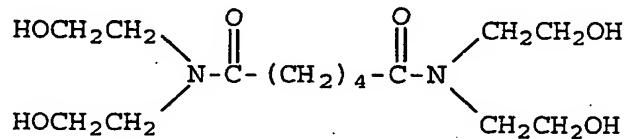
15

An oxazolinium ion can be formed *in situ* by heating an HAA at a sufficient temperature and for a sufficient time. For example, an oxazolinium ion is formed from PRIMID™ XL-552 as follows:

20

25

30



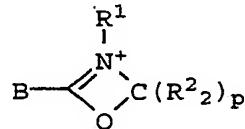
- 35 -

The cyclic oxazolinium ion then reacts with a carboxyl or amino group on a polymer chain of an SAP to form a covalent bond. A PRIMID™ XL-552 molecule then can form a second oxazolinium ion from a second 5 β -hydroxyethyl group on the molecule. This second oxazolinium ion reacts with carboxyl or amino group on a second polymer chain of the SAP, and, together with the first oxazolinium ion, forms surface cross-links. Other HAA compounds provide corresponding 10 oxazolinium ions.

The first and second oxazolinium ions generated *in situ* from an HAA molecule can be formed simultaneously. In addition, a stable oxazolinium ion can be applied directly to the surface of a SAP 15 followed by heating to surface-crosslink the SAP.

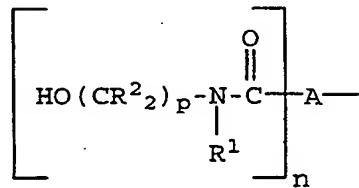
In general, an oxazolinium ion utilized in the present invention, either stable or generated *in situ* has the following general structure:

20



25 wherein B is

30



- 36 -

and A, R¹, R², p, p¹ and n are as defined above with respect to an HAA.

The SAP crosslinking solution typically contains about 0.01% to about 4%, by weight, of an oxazolinium ion precursor (e.g., an HAA) or a stable oxazolinium ion, and preferably about 0.4% to about 2%, by weight, oxazolinium ion precursor or oxazolinium ion, in a suitable solvent, for example, water, an alcohol, or a glycol. Examples of cosolvents that can be used include, but are not limited to, alcohols, e.g., methanol, ethanol, and isopropanol, and ketones, e.g., acetone. The solution can be applied as a fine spray onto the surface of freely tumbling SAP particles at a ratio of about 1:0.01 to about 1:0.5 parts by weight SAP particles to solution of oxazolinium ion or oxazolinium ion precursor.

To achieve the desired absorption properties, the HAA or the oxazolinium ion is distributed evenly on the surfaces of the SAP particles. For this purpose, mixing is performed in suitable mixers, e.g., fluidized bed mixers, paddle mixers, a rotating disc mixer, a ribbon mixer, a screw mixer, milling rolls, or twin-worm mixers.

The amount of HAA or oxazolinium ion used to surface treat the SAP particles varies depending upon the identity of SAP particles. Generally, the amount of HAA or oxazolinium ion, used to surface treat the SAP particles is about 0.001 to about 10 parts by weight per 100 parts by weight of the SAP particles. When the amount of HAA or oxazolinium ion exceeds 10 parts by weight, the SAP particles are too highly surface crosslinked, and the result-

- 37 -

ing SAP particles have a reduced absorption capacity. On the other hand, when SAP particles are surface crosslinked with less than 0.001 part by weight oxazolinium ion, there is no observable
5 effect.

A preferred amount of HAA or oxazolinium ion used to surface crosslink the SAP particles is about 0.01 to about 5 parts by weight per 100 parts, by weight, SAP particles. To achieve the full
10 advantage of the present invention, the amount of oxazolinium ion used as a surface crosslinking agent is about 0.05 to about 1 part, by weight, per 100 weight parts of SAP particles.

The formation of the oxazolinium ion
15 surface crosslinking, and drying of the surface-treated SAP particles are achieved by heating the surface-treated particles at a suitable temperature, e.g., about 90°C to about 170°C, and preferably about 100°C to about 165°C. To achieve the full
20 advantage of the present invention, the surface-treated particles are heated at about 100°C to about 160°C. At this temperature, the SAP particles are surface crosslinked with the oxazolinium ion without degrading the color of the SAP particles and without
25 increasing the residual monomer content of the SAP particles.

The surface-treated SAP particles are heated for about 60 to about 180 minutes, preferably about 60 to about 150 minutes, to effect surface
30 crosslinking. To achieve the full advantage of the present invention, the SAP particles are heated for about 75 to about 180 minutes.

- 38 -

Ordinary dryers or heating ovens can be used for heating the surface-treated SAP particles and the oxazolinium ion precursor or oxazolinium ion. Such heating apparatus includes, for example, 5 an agitated trough dryer, a rotating dryer, a rotating disc dryer, a kneading dryer, a fluidized bed dryer, a pneumatic conveying dryer, and an infrared dryer. However, any other method of forming or reacting the oxazolinium ion with the polymer of the 10 SAP particle to achieve surface crosslinking of the SAP particles, such as microwave energy, can be used. In the surface treating and surface crosslinking steps, the mixer can be used to perform simultaneous mixing and heating of the HAA or 15 oxazolinium ion, and the SAP particles, if the mixer is of a type that can be heated.

As previously stated, surface treating with an HAA or an oxazolinium ion, and subsequent or simultaneous heating, provides additional polymer crosslinks in the vicinity of the surface of the SAP particles. The gradation in crosslinking from the 20 surface of the SAP particles to interior, i.e., the anisotropy of crosslink density, can vary, both in depth and profile. Thus, for example, the depth of 25 surface crosslinking can be shallow, with a relatively sharp transition from a high level to a low level of crosslinking. Alternatively, for example, the depth of surface crosslinking can be a significant fraction of the dimensions of the SAP particle, 30 with a broader transition.

Depending on size, shape, porosity, as well as functional considerations, the degree and gradient of surface crosslinking can vary within a

- 39 -

given type of SAP particle. Depending on variations in surface:volume ratio within the SAP particles (e.g., between small and large particles), it is typical for the overall level of crosslinking to 5 vary over the group of SAP particles (e.g., is greater for smaller particles).

Surface crosslinking generally is performed after the final boundaries of the SAP particles are essentially established (e.g., by grinding, 10 extruding, or foaming). However, it is also possible to effect surface crosslinking concurrently with the creation of final boundaries. Furthermore, some additional changes in SAP particle boundaries 15 can occur even after surface crosslinks are introduced.

The surface crosslinked SAP particles of the present invention can be used as an absorbent in disposable diapers, sanitary napkins, and similar articles, and can be used in other applications, for 20 example, a dew formation inhibitor for building materials, a water-holding agent for agriculture and horticulture, and a drying agent.

Surface-crosslinked SAP particles of the present invention have advantages over conventional absorbent particles. The surface-crosslinked SAP 25 particles of the invention can be produced at a low cost by a simple method which involves mixing SAP particles with an HAA (or other oxazolinium ion precursor) or a stable oxazolinium ion, and heating. The resulting surface-crosslinked SAP particles are 30 less susceptible to fish eye formation than conventional absorbent resins and, therefore, exhibit a high rate of liquid absorption. The present surface-

- 40 -

crosslinked SAP particles also are white to off-white in color.

5 The following examples illustrate the present surface crosslinked SAP particles. It should be understood, however, that these examples are merely illustrative, and that the scope of this invention is not limited to these examples.

10 The SAP particles used in the following examples are lightly crosslinked polyacrylic acid polymers, neutralized about 75% to about 80% with sodium hydroxide. The sodium polyacrylate was made by methods well known in the art.

Example 1

15

A 2% to 50%, by weight, solution of PRIMID™ XL-552 in water was applied to the surface of the SAP particles, at the rate of 3 to 7 grams of the HAA solution per 100 grams of SAP particles.

20

The surface-treated SAP particles then were heat treated at about 150°C to about 170°C for about 60 to about 150 minutes to generate oxazolinium ions that surface crosslink the SAP particles. The best results were achieved using a greater than 10% PRIMID™ XL-552 solution applied at about 7 grams of HAA solution per 100 grams of SAP particles, then heat treating for 135 to 150 minutes at about 165°C. The performance results are summarized in Table 1.

- 41 -

Example 2

A solution containing 1% to 5%, by weight, of PRIMID™ XL-552 and 0% to 37.5%, by weight, propylene glycol in water was applied to the surface of SAP particles, at the rate of about 4 to about 10. 5 grams of solution per 100 grams of SAP particles. The surface-treated SAP particles then were heat treated at about 150°C to about 170°C for about 60 10 to about 120 minutes such that the PRIMID™ XL-552 generated oxazolinium ions to surface crosslink the SAP particles. The best results were achieved using a 3.5% PRIMID™ XL-552/25% propylene glycol solution applied at about 7 grams of solution per 100 grams 15 of SAP particles, then heat treating for about 120 minutes at 160°C. The performance results are summarized in Table 1.

Example 3

20 A solution containing 1% to 5%, by weight, PRIMID™ XL-552 and 0% to 25%, by weight, 1,3-butanediol in water was applied to the surface of SAP particles, at the rate of about 4 to about 10 grams 25 of solution per 100 grams of SAP particles. The surface-treated SAP particles then were heat treated at about 150°C to about 170°C for about 60 to about 120 minutes such that the PRIMID™ XL-552 generated oxazolinium ions to surface crosslink the SAP parti- 30 cles. The best results were achieved using a 3.5% PRIMID™ XL-552/25% 1,3-butanediol solution applied at about 7 grams of solution per 100 grams of SAP particles, then heat treating for about 120 minutes

- 42 -

at about 160°C. The performance results are summarized in Table 1.

Example 4

5

A solution containing 1% to 5%, by weight, PRIMID™ XL-552 and 0 to 25% 1,4-butanediol in water was applied to the surface of SAP particles, at the rate of about 4 to about 10 grams of solution per 100 grams of SAP particles. The surface-treated SAP particles then were heat treated at about 150°C to about 170°C for about 60 to about 120 minutes such that the PRIMID™ XL-552 generated oxazolinium ions to surface crosslink the SAP particles. The best 15 results were achieved using a 3.5% PRIMID™ XL-552/-25% 1,4-butanediol solution applied at about 7 grams of solution per 100 grams of SAP particles, then heat treating for about 120 minutes at 160°C. The performance results are summarized in Table 1.

20

Example 5

25

A solution containing 1% to 5%, by weight, PRIMID™ XL-552 and 0% to 25%, by weight, ethanol in water was applied to the surface of SAP particles, at the rate of about 4 to about 10 grams of solution per 100 grams of SAP particles. The surface-treated SAP particles then were heat treated at 150°C to about 170°C for about 60 to about 120 minutes such that the PRIMID™ XL-552 generated oxazolinium ions to surface crosslink the SAP particles. The best 30 results were achieved using a 3.5% PRIMID™ XL-552/-25% ethanol solution applied at about 7 grams of

- 43 -

solution per 100 grams of polymer, then heat treating for about 120 minutes at 160°C. The performance results are summarized in Table 1.

5

Example 6

Preparation of 1,4-Bis(N-Methyl-2-oxazolinium)butane bistosylate

10

In a dry 100 ml round bottom flask, toluene (40 mL) was admixed with bis(N-methyl-N-(2-hydroxyethyl)adipamide (2 g) and p-toluene sulfonic acid monohydrate (2.92 g) under a dry argon atmosphere. The resulting mixture was heated to reflux, and azeotropic distillation and collection in a Dean-Stark trap removed the produced water. The total reaction time was 6.75 hours. The toluene then was removed by rotary evaporation, and the residue was dried further in a vacuum oven for 60 hours at 1 Torr. The bisoxazolinium salt was an oil, and was used without further purification. The formation of the bisoxazolinium ion was confirmed by infrared spectroscopy. The bisoxazolinium salt of Example 6 was used to surface crosslink a sodium polyacrylate SAP. The results are summarized in Table 3.

30

Examples 1-5 illustrate that the scope of cosolvents (e.g., ethanol) and additional surface crosslinking agents (e.g., a diol) that can be used in combination with the HAA is broad. Examples of cosolvents include, but are not limited to, alco-

- 44 -

hols, e.g., methanol, ethanol, and isopropanol, and ketones, e.g., acetone.

An additional surface crosslinking agent can be any compound that reacts with a pendant moiety of the polymer comprising the SAP particles, and that inhibits the swell of SAP particles, can be used in conjunction with the HAA. Examples of additional surface crosslinking agents include, but are not limited to, diols, triols, polyols, e.g., ethylene glycol, propylene glycol, and 1,3-butanediol, and similar hydroxyl-containing compounds. Divalent and trivalent metal salts can be used as additional surface crosslinking agents, as swell suppressants. The HAA also can be used in combination with other surface crosslinking agents, such as EGDGE, and especially with any other surface crosslinking compound that can react with the polymer comprising the SAP particles at temperatures below 160°C.

The following Tables 1-3 summarize the performance results of specific surface crosslinked SAP particles generally disclosed in Examples 1-6 and the adsorbent properties exhibited by the surface crosslinked SAP particles. In the test results set forth in Tables 1-3, the surface-treated SAP particles were tested for absorption under load at 0.7 psi (AUL (0.7 psi)). Absorption under load (AUL) is a measure of the ability of an SAP to absorb fluid under an applied pressure. The AUL was determined by the following method as disclosed in U.S. Patent No. 5,149,335, incorporated herein by reference.

An SAP (0.160 g +/- 0.001 g) is carefully scattered onto a 140-micron, water-permeable mesh

- 45 -

attached to the base of a hollow Plexiglas cylinder with an internal diameter of 25mm. The sample is covered with a 100 g cover plate and the cylinder assembly weighed. This gives an applied pressure of 5 20 g/cm² (0.28 psi). Alternatively, the sample can be covered with a 250 g cover plate to give an applied pressure of 51 g/cm² (0.7 psi). The screened base of the cylinder is placed in a 100mm petri dish containing 25 milliliters of a test solution 10 (usually 0.9% saline), and the polymer is allowed to absorb for 1 hour (or 3 hours). By reweighing the cylinder assembly, the AUL (at a given pressure) is calculated by dividing the weight of liquid absorbed by the dry weight of polymer before liquid contact.

15 The test results in Tables 1-3 also set forth the centrifuge retention capacity (CRC) of the test samples. The centrifuge retention capacity of an SAP is a measure of the absorptive capacity of the SAP. In particular, the CRC test is a method of determining the absorbent capacity of an SAP in 20 grams of 0.9% saline (NaCl) solution per gram of polymer. This test includes swelling the SAP in a "teabag" immersed in 0.9% NaCl solution for 30 minutes, then centrifuged for three minutes. The 25 ratio of retained liquid weight to initial weight of the dry SAP is the absorptive capacity of the super-absorbent polymer, or the CRC.

The CRC test was performed as follows:

30 APPARATUS

Electronic Balance, accuracy of 0.0001 gram

Plastic Tray, 44 cm X 39 cm X 10 cm

- 46 -

Heat sealer, T-bar plastic model
Teabag material (CH DEXTER), cut and sealed to
produce a teabag 6.25 x 8.5 cm
Weigh paper or plastic weighing boat
5 Timer
Centrifuge capable of 1400 rpm, 230 mm diameter
Tongs

MATERIALS

10 SAP test sample
0.9% NaCl solution prepared with distilled or
deionized water

15 **SAMPLE PREPARATION**

(10 samples per set maximum
20 samples per 2000 ml NaCl solution)

20 a) Pour approximately 2000 ml of NaCl solution
into the tray. The liquid filling height
should be approximately 1/2 inch.

25 b) Fold teabag paper and seal two sides with heat
sealer, leaving one side open for polymer
addition. Samples may be run in duplicate
(optional).

30 c) Weight 0.2000 +/- 0.0050 grams polymer onto
weigh paper or plastic weighing boat. Record
weight and number.

35 d) Mark teabag with corresponding sample number.
Transfer polymer to teabag and close open end
with heat sealer.

40 e) Seal an empty teabag and mark it "blank."
f) Set the timer for 30 minutes. Hold each teabag
horizontally and distribute the polymer evenly

- 47 -

throughout the bag. Lay filled teabags and the blank on the surface of the NaCl solution. Submerge each teabag using a spatula to allow complete wetting. Start the timer.

5

Filled teabags were handled carefully with tongs, contacting only the edge of the teabag and not the area filled with polymer.

10

CENTRIFUGE

- 15 a) After 20 minutes soak time, remove filled teabags and blank from NaCl solution. Position the teabags in the centrifuge with each bag sticking to the outer wall of the centrifuge basket.
- 20 b) Close the centrifuge lid. Set the timer for 3 minutes. Start the centrifuge (ramp up quickly to 1400 rpm) and the timer at the same time. After 3 minutes, turn off the centrifuge (and apply the brake if necessary).
- 25 c) Weigh each filled teabag and blanks. Record weights.

30

CALCULATION

CFC (g/g) =

$$\frac{\text{final weight of teabag} - \text{final weight of blank}}{\text{dry polymer weight}}$$

35

The test results in Table 3 further set forth the Saline Flow Conductivity (SFC) of the test samples. The SFC of an SAP is a measure of the permeability of SAP particles when swollen with a liquid to form a hydrogel zone or layer. SFC measures the ability of an SAP to transport saline

- 48 -

fluids, such as the ability of the hydrogel layer formed from the swollen SAP to transport body fluids. A material having relatively high SFC value is an air-laid web of woodpulp fibers. Typically, 5 an air-laid web of pulp fibers (e.g., having a density of 0.15 g/cc) exhibits an SFC value of about 200×10^{-7} cm³sec/g. In contrast, typical hydrogel-forming SAPs exhibit SFC values of 1×10^{-7} cm³sec/g or less. When an SAP is present at high 10 concentrations in an absorbent structure, and then wells to form a hydrogel under usage pressures, the boundaries of the hydrogel come into contact, and interstitial voids in the high SAP concentration region become generally bounded by hydrogel. When 15 this occurs, the permeability or saline flow conductivity properties in this region is generally indicative of the permeability or saline flow conductivity properties of a hydrogel zone formed from the SAP alone. Increasing the permeability of 20 these swollen high concentration regions can provide superior fluid handling properties for the absorbent structure, thus decreasing incidents of leakage, especially at high fluid loadings. A method of determining the SFC value of SAP particles is set 25 forth in Goldman et al. U.S. Patent No. 5,599,335, incorporated herein by reference.

- 49 -

Table 1

Sample	Coating ¹⁾	CR ³⁾	Temp. ⁴⁾	Time ⁵⁾	CRC ⁶⁾	0.7 AUL
1	10% XL-552 ²⁾ Soln ⁸⁾	0.07	165°C	150 min.	32.4	20.2
2	25% XL-552 Soln	0.07	165°C	135 min.	29.5	23.3
3	37.5% XL-552 Soln	0.07	165°C	135 min.	30.7	22.8
4	50% XL-552 Soln	0.07	165°C	135 min.	30.4	22.1
5	5% XL-552/25% Ethanol	0.07	165°C	150 min.	31.5	26.2
6	3.5% XL-552/25% Propylene Glycol	0.07	160°C	120 min.	28.5	25.4
7	3.5% XL-552/25% 1,3-Butanediol	0.07	160°C	120 min.	31.2	26.4
8	3.5% XL-552/25% 1,4-Butanediol	0.07	160°C	120 min.	28	26.3
9 ⁷⁾	25% Propylene Glycol Only	0.07	160°C	120 min.	33.0	10.4
10 ⁷⁾	25% 1,3-Butanediol Only	0.07	160°C	120 min.	33.6	10.4
11 ⁷⁾	25% 1,4-Butanediol Only	0.07	160°C	120 min.	32.4	11.8

- 1) Surface crosslinking composition;
- 2) XL-552 is PRIMID™ XL-552;
- 3) CR is a ratio of surface crosslinking composition applied to the surface of the SAP particles, based on SAP weight;
- 4) Heating temperature;
- 5) Heating time;
- 6) CRC is retention capacity, in g 0.9% NaCl per g of dry SAP;
- 7) Samples 9-11 are comparative examples; and
- 8) All Samples 1-11 contain sufficient water to attain 100% solution weight.

- 50 -

The data in Table 1 shows that surface crosslinking using an HAA precursor for the oxazolinium ion provides surface-treated SAP particles having a greatly improved AUL (Samples 1-8) compared to SAP particles surface crosslinked only with a diol (Samples 9-11). In addition, an oxazolinium ion surface crosslinker increased the AUL, without adversely affecting the CRC, which is both beneficial and unexpected in the art.

In another test, SAP particles were surface crosslinked with PRIMID™ QM-1260 as the oxazolinium ion precursor. The results of this test, and the conditions used in the crosslinking reaction and in the tests, are set forth in Table 2. The SAP sample crosslinked with PRIMID™ QM-1260 (i.e., Sample 13) was compared to an SAP sample crosslinked with an equal amount of PRIMID™ XL-552 (Sample 12). Table 2 illustrates that an SAP surface crosslinked with PRIMID™ QM-1260 provides improved absorption properties (compare Sample 13 to control Samples 9-11).

- 51 -

Table 2

Sample #	Coating ¹⁾	CR ³⁾	Temp ⁴⁾	Time ⁵⁾	CRC ⁶⁾	0.7 AUL
12	4.9%wt XL-552, 25% propylene glycol	0.06	160°C	120 min	28.5 ¹⁰⁾	23.8
13	4.9%wt QM-1260 ⁹⁾ , 25% propylene glycol	0.06	160°C	120 min	32.4	16.5

9) QM-1260 is PRIMID™ QM-1260; and

10) CRC of control SAP particles lacking surface crosslinks is 34.3.

- 52 -

SAP particles were surface crosslinked with the stable oxazolinium salt of Example 6. The amount of oxazolinium ion used was 2000 ppm based on the weight of the SAP particle. The results of 5 these tests, and the conditions used in the crosslinking reaction and the test, are set forth in Table 3. Table 3 illustrates that an SAP surface crosslinked with a stable oxazolinium ion provides improved absorption properties (compare Samples 14 10 and 15 to control Samples 9-11).

- 53 -

Table 3

Sample #	Coating ¹⁾	CR ³⁾	Temp ⁴⁾	Time ⁵⁾	CRC ⁶⁾	0.7 AUL	SFC
14	5% Example 6 25% propylene glycol	0.04	165°C	90 min	27.1 ¹⁰⁾	23.1	44.2
15	5% Example 6 25% propylene glycol	0.04	145°C	90 min	31.5	16.7	4.6

- 54 -

Preferred SAP particles of the present invention are surface crosslinked with an oxazolinium ion and have a 0.7 AUL of at least 15, and more preferably at least 20. The preferred surface crosslinked SAP particles typically have a 0.7 AUL of about 15 to about 50. Preferred SAP particles of the present invention also have a CRC of less than 32.4, and more preferably less than 31.5. Preferred SAP particles typically have a CRC of less than 32.4 to about 25.

Preferred SAP particles of the present invention have an SFC value of at least about 15×10^{-7} cm³sec/g, and preferably at least about 20×10^{-7} cm³sec/g. To achieve the full advantage of the present invention, the SFC value of the present surface-crosslinked SAP particles is at least about 25×10^{-7} cm³sec/g, and can range to greater than 60×10^{-7} cm³sec/g.

The properties exhibited by the oxazolinium ion surface-crosslinked SAP particles illustrate that oxazolinium ion can be substituted for currently used surface-crosslinking agents, like EGDGE, and overcome disadvantages associated with such crosslinking agents, e.g., color degradation.

Obviously, many modifications and variations of the invention as hereinbefore set forth can be made without departing from the spirit and scope thereof, and, therefore, only such limitations should be imposed as are indicated by the appended claims.

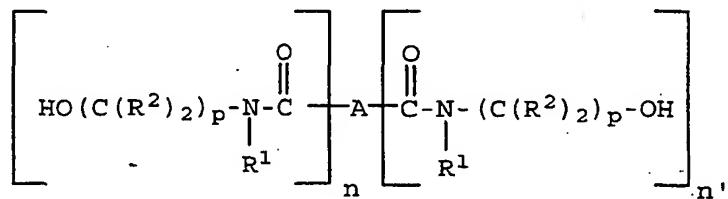
- 55 -

WHAT IS CLAIMED IS:

1. Superabsorbent polymer particles comprising 100 parts by weight of a water-absorbing resin surface crosslinked with about 0.001 to about 10 parts by weight of an oxazolinium ion, wherein the oxazolinium ion is present at surfaces of the water-absorbing resin to crosslink polymer chains at the surfaces of the water-absorbing resin.
2. The particles of claim 1 wherein the particles contain about 0.01% to about 4% parts by weight of the oxazolinium ion, per 100 parts by weight of the water-absorbing resin.
3. The particles of claim 1 wherein the particles contain about 0.4% to about 2% parts by weight of the oxazolinium ion, per 100 parts by weight of the water-absorbing resin.

- 56 -

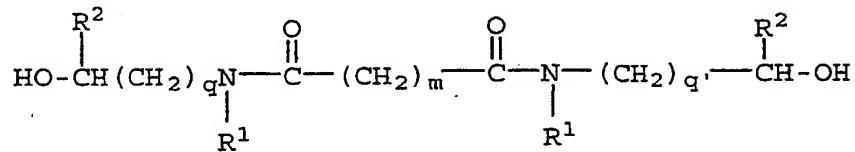
4. The particles of claim 1 wherein oxazolinium ion is derived from a precursor hydroxyalkylamide having the structure



wherein A is a bond, hydrogen, a monovalent or polyvalent organic radical selected from the group consisting of a saturated or unsaturated alkyl radical containing 1 to 60 carbon atoms, aryl, tri-C₁₋₄alkyl-eneamine, and an unsaturated radical containing one or more ethylenic groups; R¹, selected independently, are hydrogen, straight or branched chain C₁₋₅ alkyl, or straight or branched chain C₁₋₅ hydroxyalkyl; R², selected independently, are radicals selected from the group consisting of hydrogen and straight or branched C₁₋₅ alkyl, or the R² radicals are joined to form, together with carbon atoms, a cycloalkyl ring; p and p', independently, are an integer 1 to 4; n is an integer having a value of 1 or 2, and n' is an integer having a value of 0 to 2; or when n' is 0, a polymer or copolymer, wherein n is greater than 1 formed from the hydroxyalkylamide when A is an unsaturated radical.

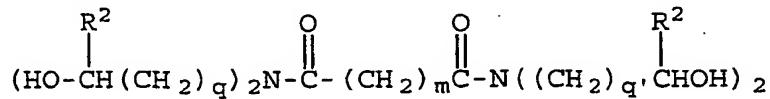
- 57 -

5. The particles of claim 4 wherein the hydroxyalkylamide has the structure



wherein R^1 is H or C_{1-5} hydroxyalkyl, m is 0-8, and one of the R^2 radicals on the beta carbon is H and the other is H or a C_{1-5} alkyl, and q and q' , independently, are an integer 1 to 3.

6. The particles of claim 4 wherein the hydroxyalkylamide has the structure

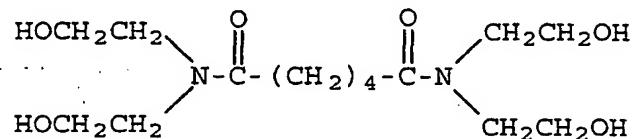


wherein both R^2 groups are H or both R^2 groups are $-\text{CH}_3$.

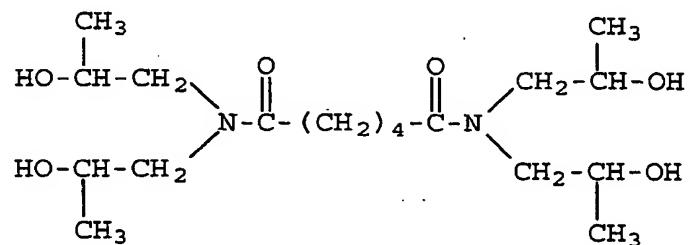
- 58 -

7. The particles of claim 4 wherein the hydroxyalkylamide is selected from the group consisting of bis[N,N-di(β -hydroxyethyl)] adipamide, bis[N,N-di(β -hydroxypropyl)] succinamide, bis[N,N-di(β -hydroxyethyl)] azelamide, bis[N-N-di(β -hydroxypropyl)] adipamide, bis[N-methyl-N-(β -hydroxyethyl)] oxamide, and mixtures thereof.

8. The particles of claim 4 wherein the hydroxyalkylamide has the structure

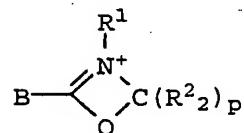


9. The particles of claim 4 wherein the hydroxyalkylamide has the structure

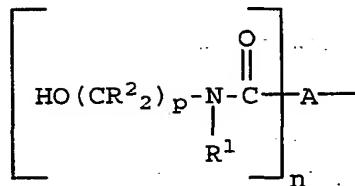


- 59 -

10. The particles of claim 1 wherein the oxazolinium ion has the structure:



wherein B is

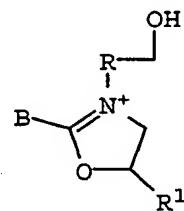


A is a bond between L's, hydrogen, a monovalent or polyvalent organic radical selected from the group consisting of a saturated or unsaturated alkyl radical containing 1 to 60 carbon atoms, aryl, tri-C₁₋₄alkyleneamine, and an unsaturated radical containing one or more ethylenic groups; R, selected independently, are hydrogen, straight or branched chain C₁₋₅alkyl, or straight or branched chain C₁₋₅hydroxyalkyl; R', selected independently, are radicals selected from the group consisting of hydrogen and straight or branched C₁₋₅alkyl, or the R' radicals are joined to form, together with carbon atoms, a cycloalkyl ring; p and p', independently, are an integer 1 to 4; n is an integer having a value of 0 to 10.

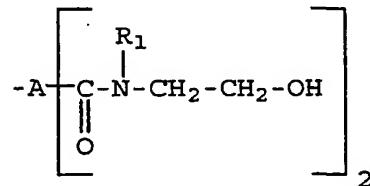
- 60 -

11. The particles of claim 10 wherein the oxazolinium ion is stable at room temperature and has sufficient reactivity to react with an acid moiety or a basic moiety at about 90°C to about 170°C to form a covalent bond.

12. The particles of claim 10 wherein the oxazolinium ion has the structure:



wherein B is



and

R¹ is H or C₁₋₅hydroxyalkyl.

13. The particles of claim 10 wherein the oxazolinium ion has a counterion ion comprising a conjugate base of an acid having a pKa of about 1.5 to about 6.

14. The particles of claim 13 wherein the acid has a pKa of about 2 to about 5.

- 61 -

15. The particles of claim 13 wherein the acid has a pKa of about 2.5 to about 4.5

16. The particles of claim 10 wherein the oxazolinium ion has a counterion selected from the group consisting of tosylate, mesylate, benzoate, haloacetate, formate, and mixtures thereof.

17. The particles of claim 1 wherein the water-absorbing resin comprises an acidic water-absorbing resin.

18. The particles of claim 17 wherein the acidic water-absorbing resin is a neutralized, lightly crosslinked acrylic-type resin containing at least 10% acidic monomer units.

19. The particles of claim 18 wherein the acidic monomer units have a carboxylate, sulfonate, sulfate, or phosphate group.

- 62 -

20. The particles of claim 17 wherein the acidic monomer units are selected from the group consisting of acidic water-absorbing resin include acrylic acid, methacrylic acid, ethacrylic acid, α -chloroacrylic acid, α -cyanoacrylic acid, β -methylacrylic acid, α -phenylacrylic acid, β -acryloxypropionic acid, sorbic acid, α -chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid, β -stearylacrylic acid, itaconic acid, citraconic acid; mesaconic acid, glutaconic acid, aconitic acid, maleic acid, fumaric acid, tricarboxyethylene, 2-methyl-2-butene dicarboxylic acid, maleamic acid, N-phenyl maleamide, maleamide, maleic anhydride, fumaric anhydride, itaconic anhydride, citraconic anhydride, mesaconic anhydride, methyl itaconic anhydride, ethyl maleic anhydride, diethylmaleate, methylmaleate, maleic anhydride, vinylsulfonic acid, allyl sulfonic acid, vinyl toluene sulfonic acid, styrene sulfonic acid, an acrylic sulfonic acid, a methacrylic sulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, 2-vinyl-4-ethylbenzene, 2-allylbenzene sulfonic acid, 1-phenylethylene sulfonic acid, sulfopropyl methacrylate, 2-hydroxy-3-methacryloxypropyl sulfonic acid, 2-acrylamide-2-methylpropane sulfonic acid, sulfated polyvinylalcohol, sulfated hydroxyethyl acrylate, sulfated hydroxypropyl methacrylate, methacryloxyethyl phosphate, and mixtures thereof.

- 63 -

21. The particles of claim 17 wherein the acidic water-absorbing resin is selected from the group consisting of a starch-acrylic acid graft copolymers, a saponified vinyl acetate-acrylic ester copolymer, a hydrolyzed acrylonitrile copolymer, a hydrolyzed acrylamide copolymer, an ethylene-maleic anhydride copolymer, an isobutylene-maleic anhydride copolymer, poly(vinylsulfonic acid), poly(vinylphosphonic acid), poly(vinylphosphoric acid), poly(vinylsulfuric acid), sulfonated polystyrene, poly(aspartic acid), poly(lactic acid), and mixtures thereof, neutralized 20 to 100 mole percent with a base.

22. The particles of claim 1 wherein the water-absorbing resin is polyacrylic acid neutralized 50 to 100 mole percent.

23. The particles of claim 1 wherein the water-absorbing resin comprises a basic water-absorbing resin.

24. The particles of claim 23 wherein the basic water-absorbing resin is a neutralized, lightly crosslinked resin containing at least 10% basic monomer units.

- 64 -

25. The particles of claim 23 wherein the basic water-absorbing resin is selected from the group consisting of a poly(vinylamine), a poly-(alkylaminoalkyl (meth)acrylamide, a polyethylenimine, a poly(allylamine), a poly(allylguanidine), a poly(dimethylallyl ammonium hydroxide), a quaternized polystyrene, a guanidine-modified polystyrene, a quaternized poly(meth)acrylamide or ester analog thereof, a poly(vinylguanidine), and mixtures thereof.

26. The particles of claim 1 wherein the water-absorbing resin comprises a mixture of an acidic water-absorbing resin and a basic water-absorbing resin.

27. The particles of claim 1 wherein the water-absorbing resin comprises multicomponent superabsorbent polymer particles.

28. The particles of claim 1 having an absorption under a load of 0.7 psi after one hour of at least 20 grams of 0.9% saline per gram of particles.

29. The particles of claim 1 having an AUL at 0.7 psi of greater than 15 and a CRC of less than 32.4.

30. The particles of claim 27 having an AUL at 0.7 psi or greater than 20.

- 65 -

31. The particles of claim 28 having a CRC of less than 31.5.

32. The particles of claim 31 having a saline flow conductivity of at least 20×10^{-7} $\text{cm}^3\text{sec/g}$.

33. Surface crosslinked superabsorbent polymer particles obtained by mixing 100 parts, by weight, of a superabsorbent polymer with about 0.001 to about 10 parts, by weight, of a hydroxyalkylamide to form surface-treated superabsorbent polymer particles, then heating the surface-treated superabsorbent particles at about 90°C to about 170°C for about 60 to about 180 minutes for the hydroxyalkylamide generate an oxazolinium ion, which forms surface crosslinks on the surface-treated superabsorbent polymer particles.

34. Surface crosslinked superabsorbent polymer particles obtained by mixing 100 parts, by weight, of a superabsorbent polymer with about 0.001 to about 10 parts, by weight, of a stable oxazolinium ion, to form surface-treated superabsorbent polymer particles, then heating the surface-treated superabsorbent particles at about 90°C to about 170°C for about 60 to about 180 minutes to form surface crosslinks on the surface-treated superabsorbent polymer particles.

- 66 -

35. A method of preparing surface cross-linked superabsorbent polymer particles comprising:

- (a) providing 100 parts by weight of superabsorbent polymer particles;
- (b) forming a solution comprising about 0.5% to about 50% by weight of a crosslinking compound selected from the group consisting of a stable oxazolinium ion, an oxazolinium ion precursor, or combinations thereof, in a solvent capable of solubilizing the crosslinking compound;
- (c) applying the solution of step (b) to surfaces of (a) to provide surface-treated superabsorbent polymer particles having about 0.001 to about 10 parts, by weight, of the crosslinking compound per 100 parts, by weight, of superabsorbent polymer particles in the vicinity of the surfaces of the superabsorbent polymer particles; and
- (d) heating the surface-treated superabsorbent polymer particles at about 90°C to about 170°C for about 60 to about 180 minutes to form surface crosslinks in the vicinity of the surface of the superabsorbent polymer particles.

36. The method of claim 35 wherein step (c) is performed prior to step (d).

37. The method of claim 35 wherein steps (c) and (d) are performed simultaneously.

- 67 -

38. The method of claim 35 wherein the crosslinking composition of step (b) further comprises a second surface crosslinking agent selected from the group consisting of a diol, a triol, a polyol, a divalent metal, a trivalent metal, a diglycidyl ether, a diamine, a halohydrin, a polyisocyanate, a dihaloalkane, a polyfunctional aziridine compound, a dialdehyde, a disulfonate ester, a diester, a multifunctional acid halide, an organic titanate, a melamine resin, a hydroxymethyl urea, and mixtures thereof.

39. The method of claim 35 wherein the second surface crosslinking agent comprises ethylene glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol, ethylene glycol diglycidyl ether, and mixtures thereof.

40. The method of claim 35 wherein the crosslinking composition of step (b) further comprises a second surface crosslinking agent capable of forming surface crosslinks on the superabsorbent polymer particles at a temperature of about 90°C to about 160°C.

- 68 -

41. A method of preparing surface cross-linked superabsorbent polymer particles comprising:

(a) polymerizing a mixture containing (i) unsaturated polymerizable monomers having acid groups or basic groups, and (ii) a polyfunctional crosslinking agent, dissolved in (iii) a solvent comprising water to form a superabsorbent polymer hydrogel;

(b) adding a sufficient amount of a crosslinking compound selected from the group consisting of an oxazolinium ion, an oxazolinium ion precursor, or a combination thereof, to the superabsorbent polymer hydrogel to provide about 0.001 to about 10 parts, by weight, of the crosslinking compound per 100 parts, by weight, of the superabsorbent polymer; and

(c) heating the product of step (b) at about 90°C to about 170°C to dry the superabsorbent polymer hydrogel, form superabsorbent polymer particles, and form crosslinks on the surface of the superabsorbent polymer particles.

42. A surface crosslinked superabsorbent polymer prepared by the method of claim 41.

43. An article comprising the superabsorbent particles of claim 1.

44. The article of claim 43 selected from the group consisting of a diaper and a catomenial device.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 December 2001 (06.12.2001)

PCT

(10) International Publication Number
WO 01/91815 A3

(51) International Patent Classification⁷:
A61L 15/60, C08F 8/30, C08J 3/24

B01J 20/26.

(74) Agent: BROWN, John, D.: Forrester Ketley & Co., Forrester House, 52 Bounds Green Road, London N11 2EY (GB).

(21) International Application Number: **PCT/IB01/01057**

(22) International Filing Date: 3 May 2001 (03.05.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/584,527 31 May 2000 (31.05.2000) US

(71) Applicant: **BASF AKTIENGESELLSCHAFT**
[DE/DE]; 67056 Ludwigshafen (DE).

(72) Inventors: MITCHELL, Michael, A.: 440 Pheasant Ridge, Lake Zurich, IL 60047 (US). ECKERT, David: 1547 South Meacham Road, Palatine, IL 60067 (US). TOMLIN, Anthony, S.: 607 Longacre Lane, Island Lake, IL 60042 (US).

(81) Designated State (national): JP.

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:
20 June 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/91815 A3

(54) Title: SURFACE-TREATED SUPERABSORBENT POLYMER PARTICLES

(57) Abstract: Surface-crosslinked superabsorbent polymer particles are obtained by treating 100 parts by weight of superabsorbent polymer particles with about 0.001 to about 10 parts by weight of an oxazolinium ion. The oxazolinium ion can be formed *in situ* by heating superabsorbent particles treated with an oxazolinium ion precursor, such as a hydroxyalkylamide. A stable oxazolinium ion also can be used to surface crosslink the SAP particle. Surface crosslinking the superabsorbent polymer particles with an oxazolinium ion increases both the rate of liquid absorption and the quantity of liquid absorbed and retained by the superabsorbent particles.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 01/01057

A. CLASSIFICATION OF SUBJECT MATTER				
IPC 7	B01J20/26	A61L15/60	C08F8/30	C08J3/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J A61L C08J C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT
--

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	US 6 239 230 B1 (D. ECKERT) 29 May 2001 (2001-05-29) the whole document	1-10, 12, 17-31, 33, 35-38, 40-44
A	WO 99 42494 A (BASF AKTIENGESELLSCHAFT) 26 August 1999 (1999-08-26) page 2, line 32 -page 3, line 12 page 9, line 40 -page 10, line 15 page 12	1-3, 17-25, 28-31, 33-37, 41-44

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

5 April 2002

Date of mailing of the international search report

19/04/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Hilgenga, K

INTERNATIONAL SEARCH REPORT

Int	tional Application No
PCT/IB 01/01057	

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 25393 A (AMCOL INTERNATIONAL CORPORATION) 27 May 1999 (1999-05-27) cited in the application page 9, line 29 -page 10, line 7 page 43, line 1 -page 46, line 21 ---	1-3, 17-28, 30, 33-44
A	EP 0 937 739 A (NIPPON SHOKUBAI) 25 August 1999 (1999-08-25) page 12, line 30 -page 13, line 31 ---	1, 17-25, 28, 43, 44
A	US 4 076 917 A (G. SWIFT) 28 February 1978 (1978-02-28) cited in the application column 1, line 30 -column 2, line 33 column 3, line 67 -column 4, line 2 ---	
A	EP 0 999 238 A (NIPPON SHOKUBAI) 10. May 2000 (2000-05-10) -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l Application No

PCT/IB 01/01057

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 6239230	B1	29-05-2001	NONE		
WO 9942494	A	26-08-1999	DE	19807502 A1	16-09-1999
			AU	2927199 A	06-09-1999
			BR	9908006 A	24-10-2000
			CA	2320778 A1	26-08-1999
			CN	1291202 T	11-04-2001
			WO	9942494 A1	26-08-1999
			EP	1056787 A1	06-12-2000
			JP	2002504566 T	12-02-2002
WO 9925393	A	27-05-1999	US	6072101 A	06-06-2000
			US	6235965 B1	22-05-2001
			US	6222091 B1	24-04-2001
			AU	1522199 A	07-06-1999
			BR	9814686 A	20-11-2001
			CA	2310691 A1	27-05-1999
			CN	1286635 T	07-03-2001
			EP	1042013 A2	11-10-2000
			FI	20001087 A	28-06-2000
			HR	20000308 A1	31-12-2000
			HU	0101141 A2	28-08-2001
			JP	2001523733 T	27-11-2001
			NO	20002546 A	20-06-2000
			PL	340959 A1	12-03-2001
			SI	20362 A	30-04-2001
			SK	7372000 A3	09-10-2000
			WO	9925393 A2	27-05-1999
			US	6159591 A	12-12-2000
			US	6342298 B1	29-01-2002
			US	2001001312 A1	17-05-2001
			US	2001029358 A1	11-10-2001
			US	2002015846 A1	07-02-2002
			US	2001044612 A1	22-11-2001
			ZA	9810461 A	17-05-1999
			US	2002007166 A1	17-01-2002
EP 937739	A	25-08-1999	EP	0937739 A2	25-08-1999
			JP	11302391 A	02-11-1999
			US	6254990 B1	03-07-2001
US 4076917	A	28-02-1978	AU	500270 B2	17-05-1979
			AU	7906075 A	16-09-1976
			BE	827169 A1	25-09-1975
			CA	1076297 A1	22-04-1980
			CH	579605 A5	15-09-1976
			DE	2509237 A1	09-10-1975
			ES	435938 A1	01-08-1977
			FR	2265801 A1	24-10-1975
			GB	1489485 A	19-10-1977
			IT	1030424 B	30-03-1979
			JP	1304064 C	28-02-1986
			JP	51017970 A	13-02-1976
			JP	60027690 B	01-07-1985
			NL	7503168 A ,B,	29-09-1975
			NO	751021 A ,B,	26-09-1975
			NZ	176822 A	06-03-1978
			SE	409117 B	30-07-1979

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IB 01/01057

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
US 4076917	A		SE 7503405 A US 4115637 A US 4101606 A US 4138541 A ZA 7501372 A	26-09-1975 19-09-1978 18-07-1978 06-02-1979 28-04-1976
EP 999238	A	10-05-2000	EP 0999238 A1 JP 2000197818 A US 6297319 B1	10-05-2000 18-07-2000 02-10-2001